

CALCIUM METAL

A. Commodity Summary

Pure calcium is a bright silvery-white metal. Under normal atmospheric conditions, however, freshly exposed surfaces of calcium rapidly become covered with an oxide layer. The metal is extremely soft and ductile, having a hardness between that of sodium and aluminum.¹ Calcium is very reactive and reacts vigorously with water, liberating hydrogen and forming calcium hydroxide, $\text{Ca}(\text{OH})_2$. Calcium does not readily oxidize in dry air at room temperature, but is quickly oxidized in moist or dry oxygen at about 300° C.²

Calcium is an excellent reducing agent, and at elevated temperatures it reacts with oxides or halides of almost all metallic elements to form the corresponding metal. Calcium is used in lead refining (for removal of bismuth), steel refining (as a desulfurizer and deoxidizer), and as an alloying agent for aluminum, silicon, and lead. Calcium is also used in the recovery of refractory metals (e.g., chromium, rare earth metals, and thorium) from their oxides and in the reduction of uranium dioxide.³

Pfizer Chem (Quigley Company), located in Canaan, Connecticut is the only domestic producer of calcium metal. Pfizer Chem uses the retort process. Calcium alloys, however, are produced by several companies, including Elkem in Pittsburgh, Pennsylvania.

B. Generalized Process Description

1. Discussion of Typical Production Processes

Calcium metal is produced by the aluminothermic method involving the high temperature vacuum reduction of calcium oxide. The raw materials for this process are limestone and aluminum. In this process, aluminum metal acts as the reducing agent. Exhibits 1 and 2 present flow diagrams for the typical process for producing calcium metal.

2. Generalized Process Flow Diagram

Aluminothermic Process

As shown in Exhibit 1, high calcium limestone, CaCO_3 , is quarried and calcined to form calcium oxide. As shown in Exhibit 2, the calcium oxide is then ground to a small particle size and dry blended with the desired amount of finely divided aluminum. This mixture is then compacted into briquettes to ensure good contacts for reactants. The briquettes are then placed in horizontal tubes, i.e., retorts, made of heat resistant steel and heated to 1100-1200°C. The open ends of the retort protrude from the furnace and are cooled by water jackets to condense the calcium vapor. The retorts are then sealed and evacuated to a pressure less than 13 Pa. After the reaction has been allowed to proceed for approximately 24 hours, the vacuum is broken with argon and the condensed blocks of about 99% pure calcium metal, known as crowns, and calcium aluminate residue are removed.⁴

¹ "Calcium," Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Vol. IV, 1992, p. 777.

² Ibid., p. 778.

³ Ibid., p. 777.

⁴ Ibid., pp. 779-780.

EXHIBIT 1
LIME AND LIMESTONE PRODUCTION

Graphic Not Available.

Source: Industrial Minerals and Rocks, 1994.

EXHIBIT 2
ALUMINUM REDUCTION PROCESS

Graphic Not Available.

Source: Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Vol. IV, 1992, pp. 777-782.

Redistillation

In applications involving the reduction of other metal compounds, a purity greater than 99% calcium is required. The necessary higher purities can be achieved through redistillation. For one method of redistillation, crude calcium is placed at the bottom of a large vertical retort made of heat-resistant steel equipped with a water cooler condenser at the top. The retort is sealed and evacuated to a pressure of less than 6.6 Pa while the bottom is heated to 900-925°C. Under these conditions calcium quickly distills to the condensing section leaving behind the bulk of the less volatile impurities. Any processing that takes place after this point must be in the absence of moisture to avoid oxidation.⁵ Redistillation does not reduce those impurities that result from volatile materials, such as magnesium. Volatile alkali metals can be separated from calcium by passing the vapors over refractory oxides such as TiO₂, ZrO₂, CrO₃ to form nonvolatile Na₂O and K₂O.⁶

3. Identification/Discussion of Novel (or otherwise distinct) Process(es)

None Identified.

4. Beneficiation/Processing Boundary

EPA established the criteria for determining which wastes arising from the various mineral production sectors come from mineral processing operations and which are from beneficiation activities in the September 1989 final rule (see 54 Fed. Reg. 36592, 36616 codified at 261.4(b)(7)). In essence, beneficiation operations typically serve to separate and concentrate the mineral values from waste material, remove impurities, or prepare the ore for further refinement. Beneficiation activities generally do not change the mineral values themselves other than by reducing (e.g., crushing or grinding), or enlarging (e.g., pelletizing or briquetting) particle size to facilitate processing. A chemical change in the mineral value does not typically occur in beneficiation.

Mineral processing operations, in contrast, generally follow beneficiation and serve to change the concentrated mineral value into a more useful chemical form. This is often done by using heat (e.g., smelting) or chemical reactions (e.g., acid digestion, chlorination) to change the chemical composition of the mineral. In contrast to beneficiation operations, processing activities often destroy the physical and chemical structure of the incoming ore or mineral feedstock such that the materials leaving the operation do not closely resemble those that entered the operation. Typically, beneficiation wastes are earthen in character, whereas mineral processing wastes are derived from melting or chemical changes.

EPA approached the problem of determining which operations are beneficiation and which (if any) are processing in a step-wise fashion, beginning with relatively straightforward questions and proceeding into more detailed examination of unit operations, as necessary. To locate the beneficiation/processing "line" at a given facility within this mineral commodity sector, EPA reviewed the detailed process flow diagram(s), as well as information on ore type(s), the functional importance of each step in the production sequence, and waste generation points and quantities presented above in this section.

EPA determined that for this specific mineral commodity sector, the beneficiation/processing line occurs between briquet pressing of calcium oxide and retorting. EPA identified this point in the process sequence as where beneficiation ends and mineral processing begins because it is here where calcium oxide undergoes a chemical change to produce calcium metal. Therefore, because EPA has determined that all operations following the initial "processing" step in the production sequence are also considered processing operations, irrespective of whether they involve only techniques otherwise defined as beneficiation, all solid wastes arising from any such operation(s) after the initial mineral processing operation are considered mineral processing wastes, rather than beneficiation wastes. EPA presents the mineral processing waste streams generated after the beneficiation/processing line in section C.2, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

Overburden. No waste characterization data or generation rates are available for overburden resulting from the mining operations. However, the overburden is likely left at the mining site.

⁵ Ibid., pp. 780-781.

⁶ Ibid.

Off-gases. The gases that result from the calciner operation are generally vented to the atmosphere, and consist primarily of CO₂ and water vapor.

2. Mineral Processing Wastes

The aluminothermic process employed at the Pfizer plant in Connecticut generates two main sources of mineral processing wastes. It is not clear whether the land surface is on or offsite. The description of the wastes does not specify whether the terms reactive and non-combustible refer to RCRA definitions.

Calcium Aluminate Wastes. The calcium aluminate is a non-reactive waste and is generally disposed of in a land surface storage area. Existing data and engineering judgment suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Dust with Quicklime. While dust collected from the system is recycled, some fugitive dust is accumulated due to contamination concerns. The dust is reactive, non-combustible, and disposed of on the land surface. This waste stream has a reported waste generation rate of 40 mt/yr.

We used best engineering judgment to determine that this waste stream may exhibit the characteristic of corrosivity. This waste stream is fully recycled and is classified as a sludge.

D. Ancillary Hazardous Wastes

Ancillary hazardous wastes may be generated at on-site laboratories, and may include used chemicals and liquid samples. Other hazardous wastes may include spent solvents (e.g., petroleum naphtha), acidic tank cleaning wastes, and polychlorinated biphenyls from electrical transformers and capacitors.

BIBLIOGRAPHY

"Calcium." Kirk-Othmer Encyclopedia of Chemical Technology. 4th ed. Vol. IV. 1992. pp. 777-782.